Two different approaches of material fabrication

1) top down approach
2) Bottom-up approach.

Top-down approach

Generally a bulk material is taken and machined it to modify into the desired shape and product.

e.g → 1) Manufacturing of integrated circuits using a sequence of steps such as crystal growth, lithography, etching, ion implantation etc.

2) Ball milling → where macrocrystalline structures are broken down into nanocrystalline structures, but original integrity of the material is retained.

3) lithographic technique.

Bottom up approach →

It is used to build something from basic materials like assembling materials from the atoms/molecules up.

e.g → i) Self assembly of nanomaterials
ii) Sol-gel technology
iii) Electrodeposition
iv) Physical and chemical vapour deposition (PVD, CVD),
(v) Epitaxial growth
(vi) Laser ablation.

p-110 → Lithography
p-161 → Ball milling

Describe — Top-down and bottom-up technique of nano mat synthesis.

→ **Top-down:** — When a bulk material is machined to modified for desired structure then it's called top-down technique.

Example, Lithography, Ball milling, manufacturing of IC.

merits: — (i) Deposition over a large substance is possible, so large scale production is possible.
(ii) chemical purification is not required.
(iii) It's very suitable for laboratory experimentation.

De-merits: — (i) It yields broad size distribution (10-100)nm.
(ii) It creates various particles shape and geometry.
(iii) Impurities such as stre defects, imperfections get introduced.
(iv) It's very expensive technique.

Bottom-up: — It's used to build something from basic materials like assembling materials from the atoms or molecular level to structure of comparatively higher size.

Example:- Sol-gel, PVD, CVD, Electro deposition, self assembly of nano materials.

merits:- (i) Accurate nanostructures can be obtained by this approach as it enables the realization of true nano scale building blocks that originate from the atomic scale.

(ii) Deposition parameters can be controlled.

(iii) Narrow size distribution is possible (1-20) nm.

(iv) Cheaper technique and less chance of contaminations of materials.

De-merits:- (i) It requires compatible surfaces.

(ii) It requires sufficient molecules, if not possible, the process cannot be possible. So, large scale production is difficult.

(iii) Stress, defect and imperfections gets introduced.

What do you mean by quantum confinement. What are the consequences of quantum confinement in different dimensional nanostructured materials.

What is a quantum Well. Give the schematic of wave functions of the first three confined states and energies of the first three confined states of an infinite depth potential.

P-710 (Lithography)
P-161 (Ball milling)

The electrodes can be made of other materials but they must be able to conduct electricity. Boron and silicon nitride nanotubes are formed by this method using elemental boron and silicon electrodes, respectively, in an activated nitrogen atmosphere [20]. An interesting variation is to make the electrodes from a mixture of conducting and nonconducting materials [21]. During heating, the nonconducting material is vaporized and ionized so that it also becomes part of the plasma arc and is transported and deposited on the cathode. Another interesting variation on plasma arcing is flame ionization. In this process, a material is sprayed into a flame and ions are produced, which can be collected and deposited in nanocrystalline form.

6.4.2 Sputtering

Sputtering is a physical vapour deposition (PVD) [22] process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions (Fig. 6.4). It is commonly used for thin-film deposition [23,24]. Standard physical sputtering is driven by momentum exchange between the ions and atoms in the material, due to collisions. In sputtering, a glow-discharge (plasma) of non-reactive ions (e.g. Ar) is created by a potential difference inside a vacuum chamber, which fall on the target (the material to be deposited) and break loose cluster of atoms and then are collected on the surface to be coated. Sputtering is one of the most versatile techniques used for the deposition of device-quality films. Compared with other deposition techniques, the sputtering process produces films with high purity and better controlled composition, provides films with greater adhesive strength and homogeneity and permits better control of film thickness [23–27]. Initially, sputtering was used to deposit thin metal films, but later, compound materials are also deposited by this method. But in these cases, target stoichiometry is a critical parameter to deposit the compound material as the sputtering rates of different elements of the compound are different. Therefore, to get proper film composition, target composition has to be chosen properly. Also, unlike normal physical sputtering, where the target material has same chemical composition as that of the deposited film, reactive sputtering technique has also been used to deposit oxide, nitride and carbide thin

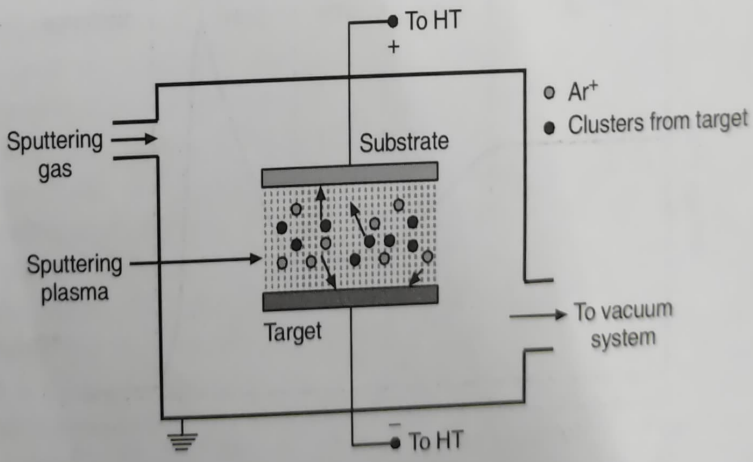


Fig. 6.4 Schematic diagram of a typical sputtering deposition system. Target and substrate are connected to two electrodes inside a vacuum chamber and Ar^+ ions bombard the target, under negative bias, and kick off the material from it and deposited on the substrate.

films. In this case, sputtering atmosphere is generally composed of a mixture of argon and oxygen/nitrogen/hydrocarbon (depending on the final product as oxide/nitride/carbide respectively) and a chemical reaction takes place inside the sputtering plasma as well as at the substrate to deposit required thin film. The substrate is generally put under an elevated temperature to enhance the reaction.

For nanostructured materials, sputtering becomes a useful tool as the material composition, thickness, homogeneity, deposition time, substrate temperature, etc. can easily be controlled by this process. Specially, deposition time and substrate temperature are the most useful parameters to deposit nanostructured materials on various substrates. Low deposition time is necessary to prevent the deposition of large number of particles to retain their nanostructure and decrease the probability of the particles to agglomerate into bigger clusters. On the other hand, low substrate temperature also prevents the agglomeration of the particles to remain in nanocrystalline form.

6.4.2.1 Sputtering in a glow discharge

Although there are several techniques available for generating the positive ions necessary for sputtering, so far, the simplest method is by establishing a glow discharge. This is usually done by setting up a high potential difference between two flat electrodes in a low-pressure (10^{-2} to 10^{-3} Torr) gas. There are several types of gas discharge, and the type, which is observed between two electrodes, depends upon several factors: the pressure of the gas, the applied voltage, the electrode configuration etc., which influence the path length of the discharge and its current density. Figure 6.5 shows the I-V characteristics of a discharge between two flat plates in a gas with a pressure in the range of several mTorr to several hundred mTorr. There is no appreciable current below some minimum voltage at which the gas breaks down abruptly. This region is known as 'Townsend Discharge', and the current may be increased within this region without any change in voltage. As the current is increased further, however, additional carriers are

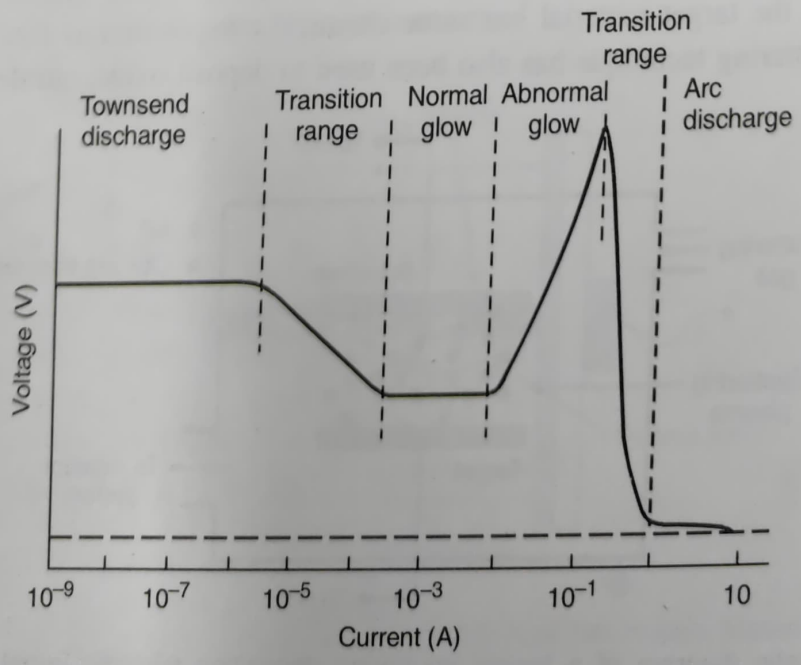


Fig. 6.5 Voltage–Current graph of a gas discharge. The voltage is represented by a linear scale and current by a logarithmic scale.

Lithography

Lithography is one of the important top-down technique where chemical process is used to create an image for printing purpose. There are two types of lithography process — (i) photo or optical lithography (ii) particle beam lithography.

(i) photo lithography:- In photo lithography visible and u-v radiation are employed used to transfer a geometric pattern from a photo mass to a light sensitive chemical (photoresist) on the substrate. Depending on the pattern on the photo mass different type of structure can be generated.
on the substrait which further used in photonic and electronic divices. In u-v lithography radiation of wave length (10 - 14) nm are used to achieve small featured sized devices (≤ 5nm)
Now adays, photo lithography, D-uv light with wavelength of (248-193) nm to create featured size down to 50 nm.

(ii) particle beam lithography:- In particle beam lithography Particle beams does not undergo diffrection and scattering is minimize. In this case high resolution can be achieved. since, high vacume should be maintain in this process it be comes expensive method. But it can makes pattern of featured size less than 1 nm. Due to very slow speed this type of lithography cannot be commerially used in industry but found wide uses in research.
It is used in mass making and low volume production of semiconductor components.

This technique can fabricate to the limit of 1-D and 0-D nano structure of very small size.

In Lithography high vaccume should be maintain throughout the whole process to avoid contramination.

Ball milling

It is one of the top-down method. capable of producing nanoscale material by mechanical crassing process. It is used for down sizing micrometer size powders to nanoscale. In this process small balls are allowed to rotate around the inside of a drum and drop with gravity force onto a solid enclosed in the drum. The K.E of the Grinding medium is transfered to micrometer sized grained metal, alloys, ceramics etc. whose nano-crystalytes are produce, the sample is placed in a canic star which is made to rotate at high revolution per minuite. The whole process is done under control atmospheric condition to prevent oxidation.

The significant advantage of this method is that it can be readly implemented commertially. During this process seriour plastic deformation of the sample material leads to the formation of defects and dislocation, which are subjected to mechanical deformation shear and strain condition. Another drawback of this method is contramination can occure at certain particle size.

Example:- It is used to makes carbon base materials nano tube, oxides powderete like La_2O_3, SnO_2, $BaTiO_3$, FeO, TiO_2 etc.

Thermal deposition

Evapuration deposition of thin films is a process where the material to be deposited is heated to a high vapour pressure in vaccume when heating of the material is done by electrically resisbivity (Joule heating) it's called thermal evapuration.

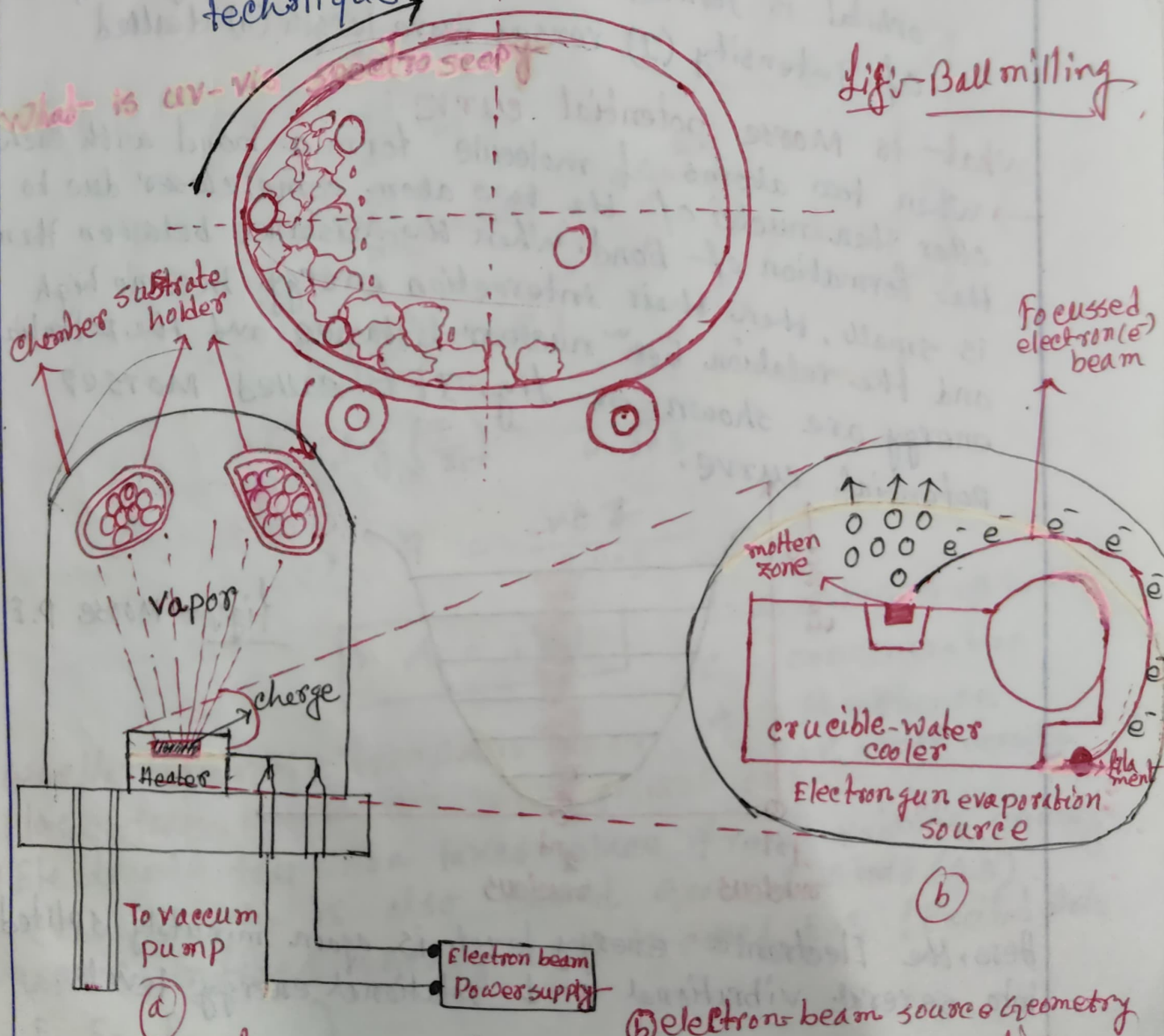
It is one of the basic technique for thin film growth used for surface metalization.

Fig shows the ~~schematic~~ schematic of thermal evapuration chamber where a filament of high current (40-100)A is used to purpose (for producing suffitient amount of thermal energy). When the target material is heated adiquently it begins to evapurate. And travels through the chamber and deposite on the substrait to be coated. The higher the vaccum ~~the~~ more efficiently the material will be deposited to the substrained/substrate to the higher vaccum. Because in higher vaccum there are less no of molecule in the chember which will increase mean free path and a longer mean free path will allow the evapurated molecule to travel further before striking an unwanted molecule in the chamber.

So, the rate of deposition depends upon the current being passed through the filament and also on vapour pressure inside the chamber.

Advantages:- Ease of deposition the K.E of the emaneted specis from the source is less than 5 ev and hence higher degree of crystalinity in films grown cannot be expected in this technique.

Fig:- Ball milling



(b) electron-beam source Geometry

Fig:- (a) Thin-film deposition by thermal evaporation.

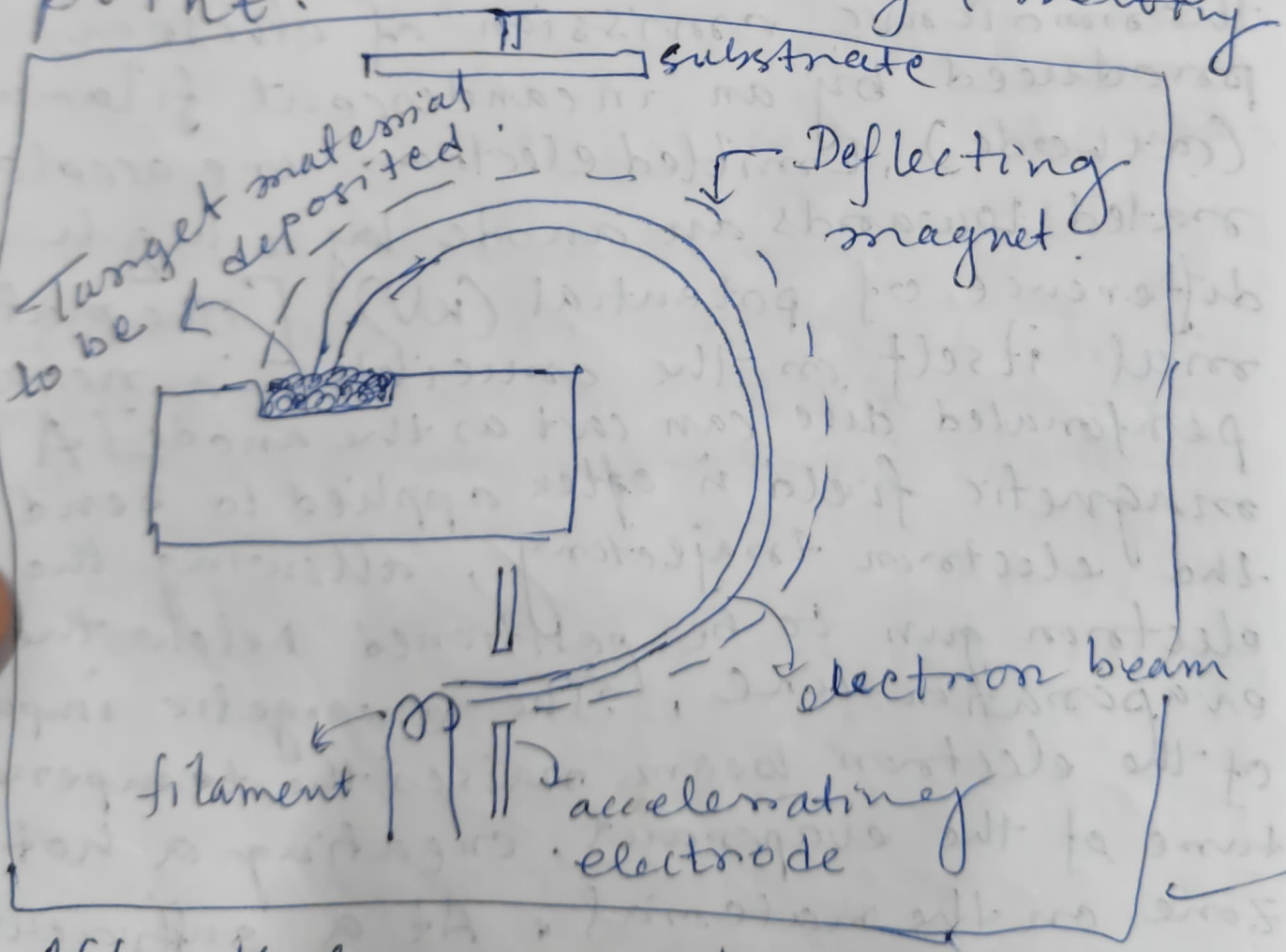
e-beam evaporation:-

When the heating of the material to be deposited on the substrate in evaporative deposition method is done by high energy electron beam bombardment, it is called e-beam evaporation process.

The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by an incandescent filament (cathode). Emitted electrons are accelerated towards an anode by a high difference of potential (kV). [The material itself or the crucible or a near perforated disc can act as the anode]. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. The energetic impact of the electron beam raises the temperature of the evaporant, creating a hot zone on the material. At a sufficiently high temp., the material will begin to

Fig. 6.5 Voltage–Current graph of a

evaporate. As electrons can be localized, it is possible to obtain a much localised heating on the material to evaporate with a high density of evaporation power (several kW). This allows controlling the evaporation rate, from low to high ~~energy~~ value and chance of depositing materials with high melting point.



After that evaporated material is deposited on the substrate.

Pulsed Laser Deposition:-

Pulsed Laser Deposition (PLD) technique is used for thin film deposition as well as nano material synthesis. In this process, a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired material and composition to vaporise the target and deposit materials on a substrate.

The deposition generally takes place in ultra high vacuum or in the presence of some background gas of certain pressure. Some neutral gases such as Ar are used at some desired pressure to control the deposition rate as well the film composition whereas reactive gases like oxygen or nitrogen are sometimes used to deposit oxide or nitride materials. P.T.O

→ Electron beams are accelerated from a heated filament towards the source by accelerating anodes and a magnetic field. Due to bombardment of highly energetic electron beam, local heat is generated at the source, which evaporates the materia

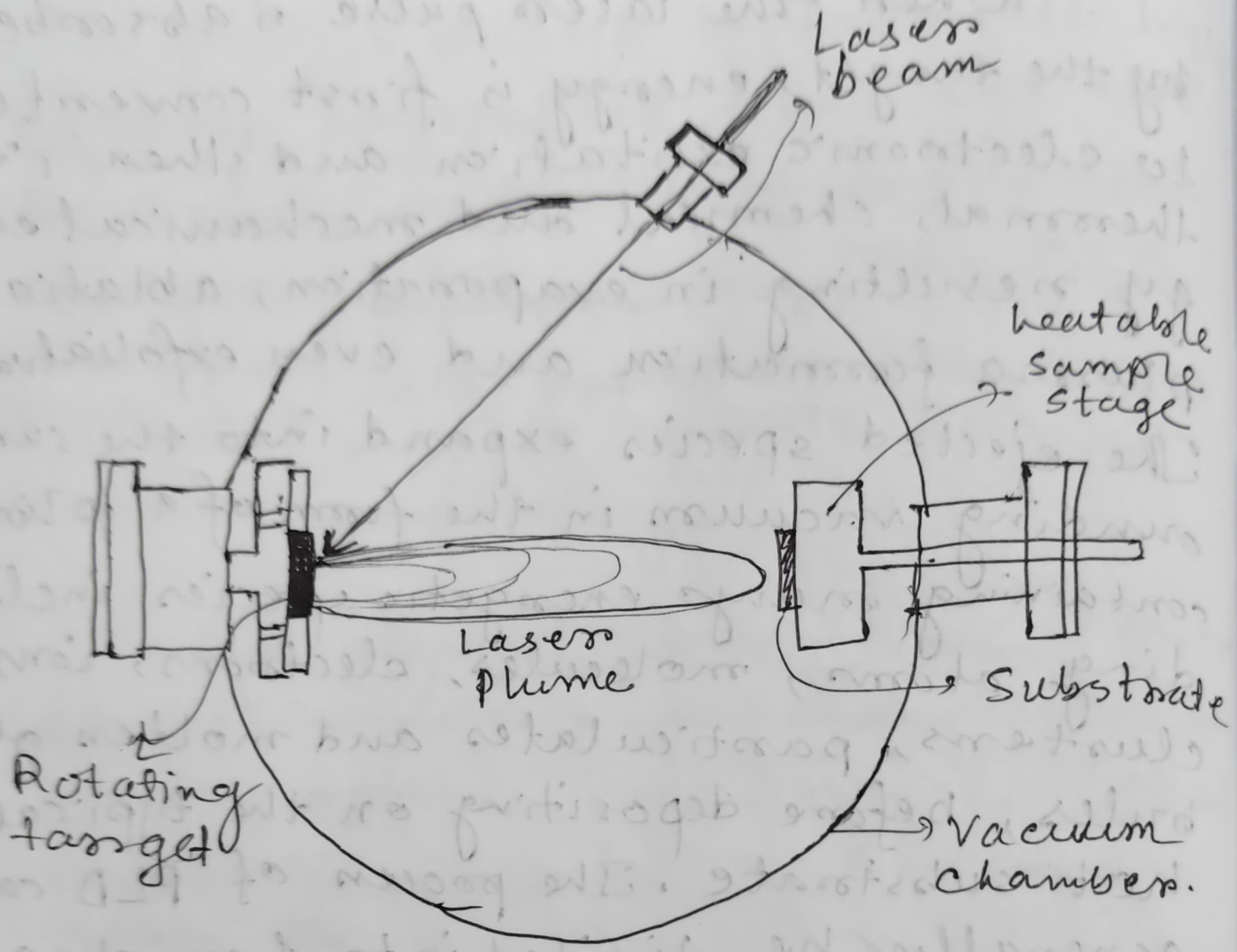
PLD is utilised to fabricate high quality crystalline films and also to deposite materials of complex stoichiometry (e.g. superconducting $YBa_2Cu_3O_7$ thin films) like multi-element oxides, nitrides, metallic multilayers and various superlattices.

The physical phenomena of laser-target interaction and film growth are quite complex. The target material which is evaporated by the laser is normally found as a rotating disc attached to a support. It can be sintered into a cylindrical rod with rotational motion and a translational up and down movement along its axis.

PLD relies on a photon interaction to create an ejected plume of material from any target. The vapour involves (plume) is collected on a substrate placed a short distance from the target.

When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate. The process of PLD can generally be divided into four stages:

i) Laser ablation of the target material and creation of a plasma
ii) Dynamics of the plasma
iii) Deposition of the ablation material on the substrate
iv) Nucleation and growth of the film on the substrate surface.



Basic Step up of PLD system.

* Laser beam is collimated through lenses to the target for ablation.
* Target can be rotated
* A laser plume is generated between target and the substrate
* The substrate can be rotated as well as heated (if needed) for uniform film deposition.

Chapter

6 Synthesis of Nanomaterials—Chemical Methods

6.1. INTRODUCTION

In the previous chapter we have discussed various physical methods for the synthesis of nanostructure materials. Physical methods in general, require high vacuum and high temperatures and need expensive pumps and gauges and deposition chambers. Hence these methods are expensive methods for the synthesis of nanomaterials. Since the deposition takes place in ultra-high vacuum chambers, hence purity of end products can be obtained. These methods therefore lead to less contamination by impurities.

Chemical methods for the synthesis of nanomaterials are the subject matter of this chapter. These methods such as chemical vapour deposition, especially MOCVD, Sol-Gel process, electrodeposition, hydrothermal synthesis, spray pyrolysis, colloidal synthesis etc. work on temperatures lower than that required for physical methods. Further there is no requirement of high vaccum chambers and hence need inexpensive instrumentation. As a result, these methods provide cost effective synthesis of nanomaterials as compared to physical methods. **Chemical methods are suitable for large scale production**. These methods involve simple techniques. But there are possibilities of foreign atoms (ions) being adhered to the desired films or materials. Hence more contamination than physical methods results into **less purity of end products.**

6.2. CHEMICAL VAPOUR DEPOSITION

Chemical vapour deposition (CVD) is a **bottom-up approach** for the synthesis of nano-structured materials. It is a chemical process that is used to produce high quality, high performance, solid materials. In semiconductor industry, CVD is used to produce thin films. Micro fabrication processes widely use CVD to deposit materials in various forms such as monocrystalline, polycrystalline, amorphous and epitaxial etc. These materials include silicon (oxide, carbide, nitride etc.), carbon (fiber, nanofibres, nanotubes, diamond and graphene), fluorocarbons, filaments, tungsten, titanium nitride and various dielectrics with high dielectric constants.

In CVD processes, the wafer (substrate) is exposed to one or more **volatile precursors**, which react and/or decompose on the substrate surface to produce the

desired deposit (fig. 6.1). The process of decomposition can be assisted or accelerated by the use of heat, plasma, or other processes. The form of **the precursor can be a gas, liquid, or solid**. Gaseous precursors are introduced into the chamber at normal pressures and temperatures while solids and liquids require high temperatures and/or low pressures. CVD processing temperatures are high, typically in the range 850 to 1100°C. In this process some volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Basic steps in the CVD processes may be summarized as follows :

- Formation of the reactive gas mixture
- Mass transport of the reactant gas through a boundary layer to the substrate
- Adsorption of the reactants onto the substrate
- Reaction of the adsorbents to form the deposit.

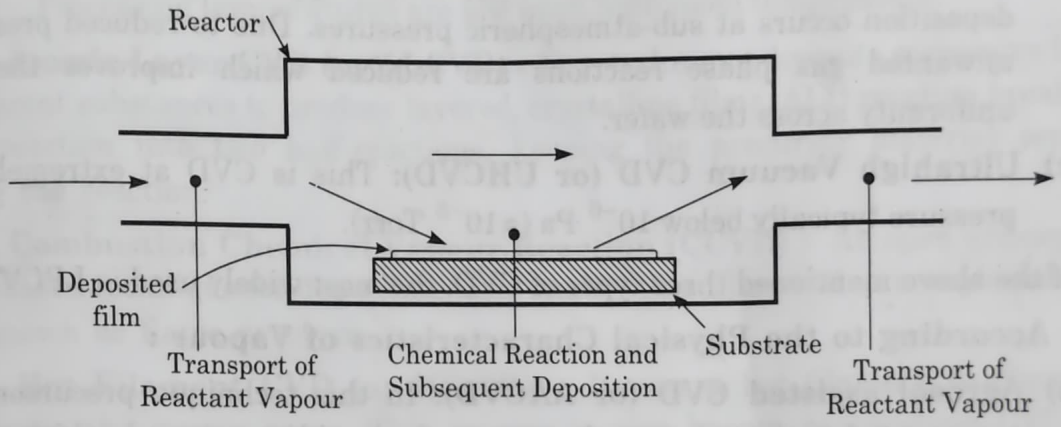


Fig. 6.1. CVD Apparatus

Pretreatment of the substrate is required. The reaction chamber must be clean, leak tight, and free of dust and moisture. Most commonly used metals in CVD coatings are: nickel, tungsten, chromium, titanium carbide etc.

Uses and Applications

- Chemical vapour deposition is **suitable for large area thin film deposition**. It is used for corrosion and wear resistance and applied on materials to acquire specific properties.
- CVD is used to deposit high quality films and augment substrate surfaces in ways which cannot be done by traditional surface modification techniques such as electroplating, painting etc. It is extremely useful in the process of atomic layer deposition (ALD) for depositing extremely thin layers of material.
- GaAs films deposited by this technique are used in some integrated circuits (ICs) and photovoltaic devices. Amorphous polysilicon prepared through CVD is also used in photovoltaic devices. Polymerization by CVD allows for super thin coatings which possess some very desirable qualities such as lubricity, hydrophobicity and weather resistance.

Physical methods are expensive but relatively more reliable and reproducible. Most of the chemical methods are cost effective, but their full potential for obtaining device-quality films has not been completely explored in many cases.

6.5. SOL-GEL PROCESS

It is a **bottom-up approach** of synthesis which is in use since late 1800s. The modern sol-gel technique started around 1970s. It is an example of liquid phase synthesis. A sol is a colloidal or molecular suspension of solid particles or ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network. Sol-gel is a **multi-step chemical solution process** (i.e. a wet chemical technique) widely used recently in the fields of materials science and ceramic engineering to make ceramic and glass materials in the form of thin films, fibers, or powders.

The process of sol-gel generally starts with the mixing of metal alkoxides or salts in water or in a suitable solvent (in most cases alcohol) at ambient or slightly elevated temperatures. Thus metal alkoxides and metal chlorides are typical precursors in this process which undergo hydrolysis and polycondensation reactions. The most widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes (TEOS) which form silica gels. Alkoxides are immiscible in water. They are organometallic precursors for silica, aluminum, titanium, zirconium and many others. In the process metal-oxo or metal-hydroxo polymers are formed.

In sol-gel process it is **very important to control the pH of the starting solution** to avoid the precipitation as well as to form the homogeneous gel, which can be achieved by the addition of base or acidic solutions. Organic compounds with hydrophilic functional groups in small molecules such as citric acid, succinic acid, oxalic acid, tartaric acid etc. and polymers (*e.g.* polyacrylic acid and polyvinyl pynolidine) can be used with metal ion sources to form the sol as well as control the particle size and uniformity of the products. **A catalyst is used to start the reaction and control pH of the solution.**

Sol-gel formation occurs in four stages:

1. Hydrolysis
2. Condensation
3. Growth of particles
4. Agglomeration of particles.

These processing steps are discussed below :

Hydrolysis : In hydrolysis, addition of water replaces alkoxy groups [OR] with hydroxyl groups [OH]. Hydrolysis occurs by attack of oxygen on silicon atoms in silica gel. A catalyst such as HCl and NH_3 accelerates the hydrolysis. Hydrolysis

continues until all [OR] groups are replaced by [OH-] groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si), alcohol and water.

Condensation : Polymerization to form siloxane bond occurs by either a water producing or alcohol producing condensation reaction. Condensation reaction finally results in the formation of monomer, dimer, cyclic tetramer, and high order rings. Hydrolysis rate is influenced by pH, reagent concentration and H_2O/Si molar ratio. Ageing and drying are also important steps. By controlling these factors the structure and properties of sol-gel derived inorganic networks can be varied.

Growth and Agglomeration : With increase in the number of siloxane bonds, the molecules aggregate in the solution, where they form a network and then a gel is formed upon drying. The water and alcohol are driven off and the network shrinks. For pH values greater than 7 and H_2O/Si value ranging from 7 to 5, spherical nanoparticles are formed. The reactions involved are as follows:

$$2\,HOSi(OR)_3 \longrightarrow (OR)_3\,SiOSi(OR)_3 + H_2O$$

or

$$2\,HOSi(OR)_3 \longrightarrow (OR)_2OH\,Si\,O\,Si\,(OR)_3 + H_2O$$

For pH > 7, silica is more soluble and silica particles grow in size. The growth of particles stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. **Higher temperatures result in the formation of larger particles.**

Advantages of Sol-Gel Technique

- Sol-gel method of thin film deposition is a cheap and low temperature technique with fine control on the chemical composition of the product.
- It is able to produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel.
- By this process we can get at low temperature, high density glass without high temperature re-crystallization.
- Smaller particle size and morphological control in powder synthesis.
- It can produce thin bond coating to provide excellent adhesion between the metallic substrate and the top coat.
- This process is able to coat onto large or complex shape objects.
- Sol-gel process can produce thick coating to provide corrosion protection performance.
- This process can have low temperature sintering capability, usually in the range 200-600°C
- Sol-gel is a versatile process as it can produce aerogels, xerogels, ceramic materials, nanopowders, nanorods and nanostructured thin films etc.

Disadvantages of Sol-Gel Technique

- The cost of the raw materials (i.e. chemicals) may be high as compared to mineral based metal ion sources
- Products would contain high carbon content when organic reagents are used in preparative steps and this would inhibit densification during sintering
- There is often a large volume shrinkage and cracking during drying due to the generation of large capillary stresses
- It is difficult to avoid residual porosity and OH-groups
- Being a multi-step process, close monitoring is required
- The process is not very clean. It contains undesired atoms, molecules, ions etc. This deteriorates electrical and optical properties of deposited material.

Applications

- Sol-gel process has been extensively used for forming coatings on window glass
- It can be used to produce powders and fibers
- Sol-gel technique can be used to deposit films and coatings on a range of different surfaces, enabling a flexibility which is not available in many vapour phase methods
- It is used in drug delivery systems
- In making ultraviolet (UV) protection gels
- For producing lubricants and scratch free paints
- In developing new fire retardant materials.

6.6. ELECTRODEPOSITION

Electrodeposition is a **liquid phase** chemical method of synthesis of nanostructured materials. It belongs to the category of **bottom-up approach** of synthesizing nanomaterials. Thin films have been extensively used in microelectronics. There are numerous and growing applications in communications, optical electronics, coatings of all kinds and in energy generation. Electrodeposition is a long established method to deposit metal layers on a conducting substrate. Ions in the solution are deposited onto the negatively charged cathode, carrying charge at the rate which is measured in the form of a current in the external circuit. The layer thickness is a function of current density and the time for which the current flows. The deposit can be detached if the substrate is chosen to be soluble by dissolving it away (Fig. 6.3).

Electrodeposition is the **most suitable technique for depositing nanostructured thin films from aqueous solution** served as samples under investigation. It is particularly suited to the fabrication of heterojunctions simply through a change in the deposition electrolyte. Electrodeposition of metallic layers

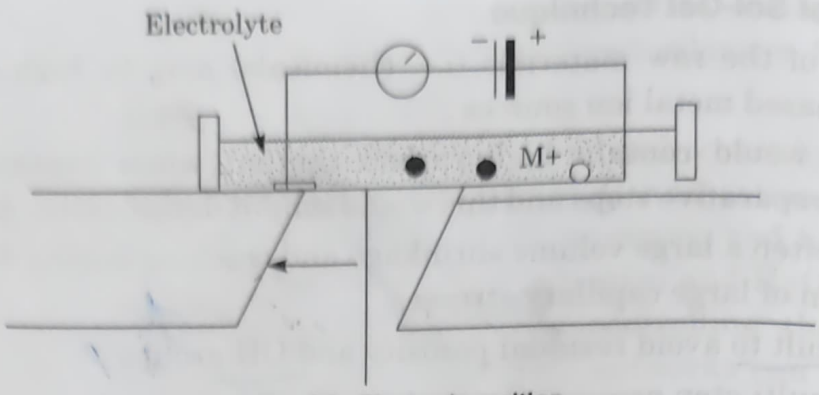


Fig. 6.3. Electrodeposition

from aqueous solution is based on the discharge of metal ions present in the electrolyte at a cathode surface (the substrate or component). The metal ions accept an electron from the electrically conducting material at the solid-electrolyte interface and then deposit as metal atoms onto the surface. The electrons required for this purpose are either supplied from an externally applied potential source or are surrounded by a reducing agent present in solution (electroless reduction). The metal ions are derived either from metal salts added to solution, or by the anodic dissolution of the so-called **sacrificial anode** which is made of the same metal that is to be deposited at the cathode.

Electrodeposited thin films are mechanically strong and uniform. It has been observed that certain properties of nanostructured deposits such as hardness, wear resistance and electrical resistivity are strongly affected by the grain size. A combination of increased hardness and wear resistance gives superior coating performance. Nanocomponents fabricated using electrodeposition include wires consisting of alternating magnetic and non-magnetic layers each only a few nanometers thick and single-electron transistors (SETs) using niobium. A slow electrodeposition process will produce a better finished product.

Advantages

- Electrodeposition is relatively cheap and fast process and allows complex shapes
- It has high utilization rate of the raw materials
- Low energy consumption process
- Low material waste
- Ease of implementation and room temperature operation
- An exceptionally versatile process
- Precise control of film thickness, morphology, stoichiometry, doping etc. is possible
- Isothermal technique which avoids the negative effects of inter-diffusion, contamination, and dopant redistribution.

Applications

- Electrodeposition has three main characteristics that make it so well suited for nano-, bio- and microtechnologies. These characteristics are-
- Electrodeposition can be used to grow functional material through complex 3D masks.
- It can be performed near room temperature from water-based electrolytes.
- This process can be scaled down to the deposition of a few atoms or up to large dimensions.

Besides continuing traditional applications, new applications of electrodeposition will emerge rapidly, especially in the fields of nanoelectronics, biotechnology, and energy engineering. Some specific applications of electrodeposition are as follows:

- Polymers and biomaterials are electrodeposited for biomedical applications
- Metal oxides and compound semiconductors are grown electrochemically for electronic or optoelectronic applications.

6.7. SPRAY PYROLYSIS

Spray pyrolysis is a **non vacuum technique** suited to deposit wide variety of thin and thick films, ceramic coatings and powders etc. It belongs to the category of **bottom-up methods** of synthesizing nanomaterials. Spray pyrolysis is an example of **gas phase synthesis**. Films **deposited** by this technique were used in devices such as solar cells, sensors and solid oxide fuel cells.

In spray pyrolysis a thin film is deposited by spraying a solution (by forcing it through a hole or nozzle at high pressure) on a heated surface, where the constituents react to form a chemical compound (fig. 6.4). The substrate is heated to about 350-500°C. The precursors (in liquid or gaseous form) in this process are vaporous. The reactants are selected such that the products other than the desired compound (*i.e.* by-products) are volatile at the temperature of deposition (*i.e.* substrate surface temperature).

"Spray pyrolysis is the aerosol process that atomizes a solution and heats the droplets to produce solid particles".

Aerosol is defined as a suspension of solid or liquid particles in a gas. Atomization is the production of droplets and their dispersion into the gas. Spray pyrolysis takes place in the following steps:

(i) Aerosol generation and transport

(ii) Droplet impact with consecutive spreading

(iii) Precursor decomposition.

Spray pyrolysis is **particularly useful for the deposition of oxides** and has long been a production method for applying a transparent electrical conductor of

SnO_x to glass. Properties of deposited thin films depend on the preparation conditions. The most critical parameter involved in spray pyrolysis is the substrate surface temperature which influences film roughness, cracking, crystallinity etc. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure. Temperature also affects optical and electrical properties of deposited films.

Equipments Needed

1. Atomizer : It is an instrument that carries out atomization which means production of droplets and their dispersion into the gas. Atomizer may be of any one of the three types:

(i) Air blast type
(ii) Ultrasonic type, and
(iii) Electrostatic type.

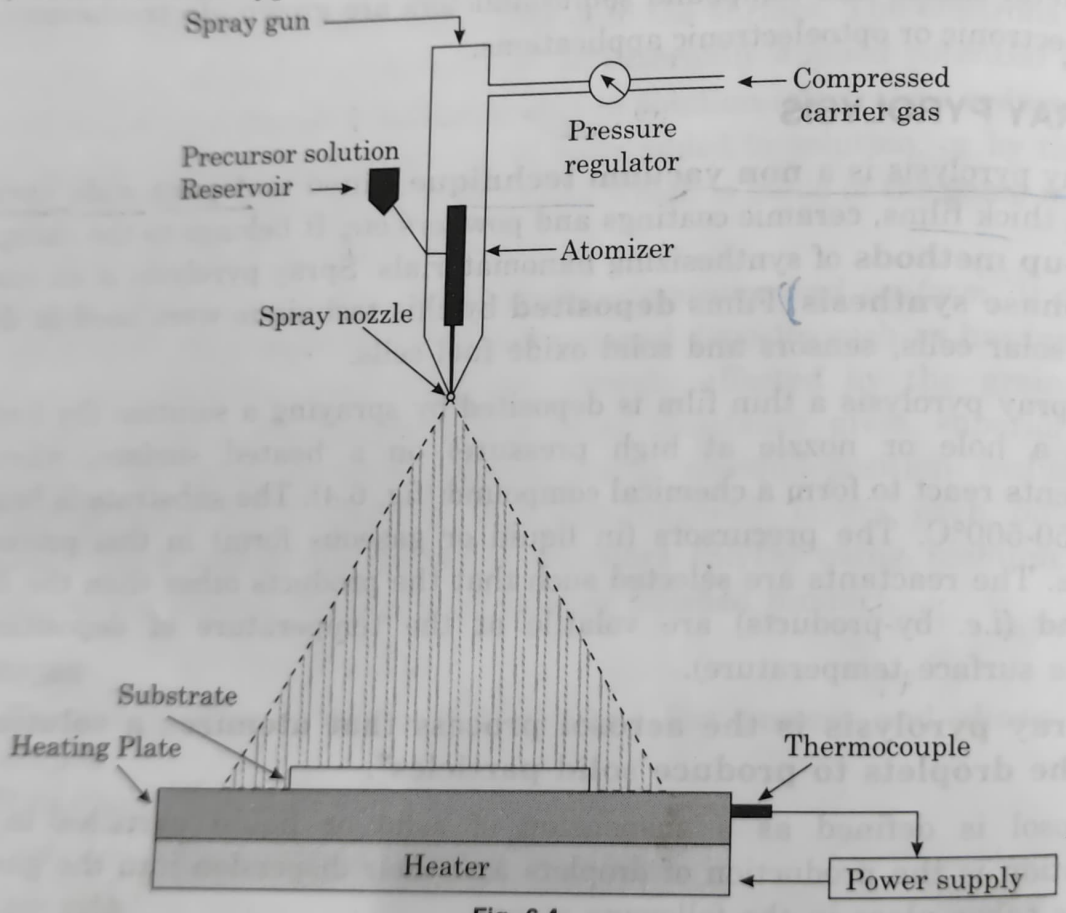


Fig. 6.4.

2. Precursor solution : Chemicals used in the reaction are called precursors.

3. Substrate heater : An arrangement for heating the substrate in the temperature range 350-500°C.

4. Temperature controller : Arrangement for maintaining the temperature in the specified range.

According to the type of reaction involved, chemical spray deposition processes may be classified into four categories as follows:

(i) Process A : The droplet resides on the surface as the solvent evaporates, leaving behind a solid that may further react in the dry state.

(ii) Process B : In this process the solvent evaporates before the droplet reaches the surface and the dry solid impinges on the surface, where decomposition takes place.

(iii) Process C : The solvent evaporates as the droplet approaches the substrate; the solid then melts and vaporizes and the vapour diffuses to the substrate. A heterogeneous reaction occurs at the substrate.

(iv) Process D : In this case the whole reaction takes place in the vapour state.

Advantages

- Spray pyrolysis is a simple, relatively cost effective, non vacuum processing method for large area applications
- It is an extremely easy technique for preparing films of any composition
- The process involves continuous operation with high yield
- It does not require high quality substrates or chemicals.

Disadvantages

- Spray pyrolysis often results in aggregates and agglomerates rather than singleton primary particles.

Applications

- In the deposition of dense films, porous films, and for powder production
- Multilayered films can also be deposited using this technique
- In glass industry and solar cell production.